New mineralogical data on polymetallic mineralization in the Gierczyn-Przecznica area, SW Poland

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Introduction

Both tin and cobalt, elements not often found together, were mined in the Stara Kamienica Schist Belt (SKSB) in SW Poland. The tin ores were mainly exploited from the 16th to 18th centuries while the cobalt was exploited in the 18th and 19th centuries (maximum annual production reached 2200 tonnes of ore, Michniewicz et al. 2006). The 1930s and 1940s were times of renewed interested in these deposits and subsequently, the first detailed geological investigation was done in the 1950s with exploration based on the existing mine workings and drill core. However, no mining eventuated because the resources and grades were deemed uneconomic.

Nonetheless, due to the unique character of these ores and diverse mineralogy, reflecting a complicated geological evolution, they can provide new insight into the formation of tin and cobalt deposits in metamorphosed terranes.

The aim of this study was to investigate and characterize the sulfide mineralization in this area, with a particular focus on elements which might constitute potential by-products such as indium and silver.

Geological setting

The Karkonosze–Izera Massif (KIM) is located in the south-central part of the West Sudetes on the NE margin of the Bohemian Massif, located in Poland and Czech Republic (Fig. 1). The KIM consist of the Karkonosze Granite intrusion and its metamorphic envelope. These granites crystallized around 312-307 Ma and are considered to be post-collisional, transitional between I- and S-type, mostly peraluminous, strongly evolved and fractionated (Mikulski 2007; Mikulski et al. 2020). The metamorphic envelope of the intrusion includes four different structural units of Neoproterozic–Paleozoic age: the Izera–Kowary Unit (IKU), the Ještĕd Unit, the Southern Karkonosze Unit and the Leszczyniec Unit. The Izera–Kowary Unit, separated by the Karkonosze pluton into northern and southern parts, consist of gneisses and mica schists. The northern part is the Izera Massif comprising texturally diverse Izera Gneisses formed during metamorphism and deformation in the Late Devonian to Early Carboniferous. The Izera Complex also contains three schist belts: the northern Złotniki Lubańskie, the central Stara Kamienica and the southern Szklarska Poręba belts. They are composed mostly of mica schists with minor interbeds of amphibolites, calc-silicate rocks, quartzites and quartz–feldspar schists, and were metamorphosed under the conditions of upper greenschist and lower amphibolite facies.

Low-grade cassiterite mineralization is disseminated in the chlorite–mica–quartz schist (in some cases also rich in almandine garnet) forming a set of parallel stratabound bodies that are accompanied by a polymetallic sulphide/sulphosalt association with the dominance of chalcopyrite and pyrrhotite (e.g. Piestrzyński and Mochnacka 2003; Michniewicz et al. 2006; Mochnacka et al. 2015) (Fig. 2).

The origin of mineralization is still a matter of discussion and several genetic models have been proposed (for a detailed reference list see Michniewicz et al. 2006 and Mochnacka et al. 2015). The most widely accepted model involves hydrothermal activity attributed to the Ordovician, granitic protolith of the Izera Gneisses or the Variscan Karkonosze Granite.

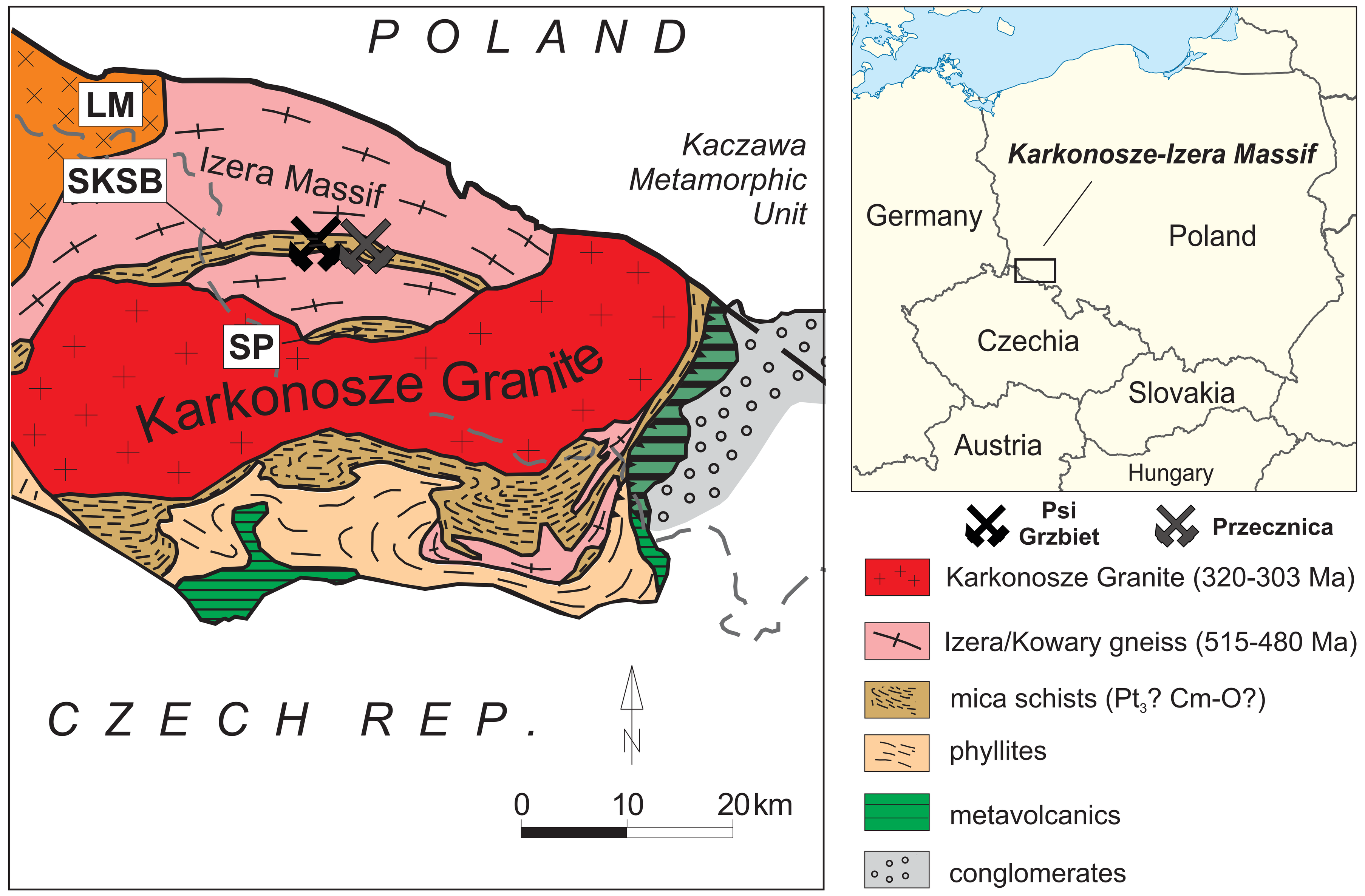

Figure 1. Geological map of the Karkonosze-Izera Massif, LM – Lausitz Massif, SKSB – Stara Kamienica Schist Belt, SP – Szklarska Poręba Belt (modified from Mazur et al. 2010).

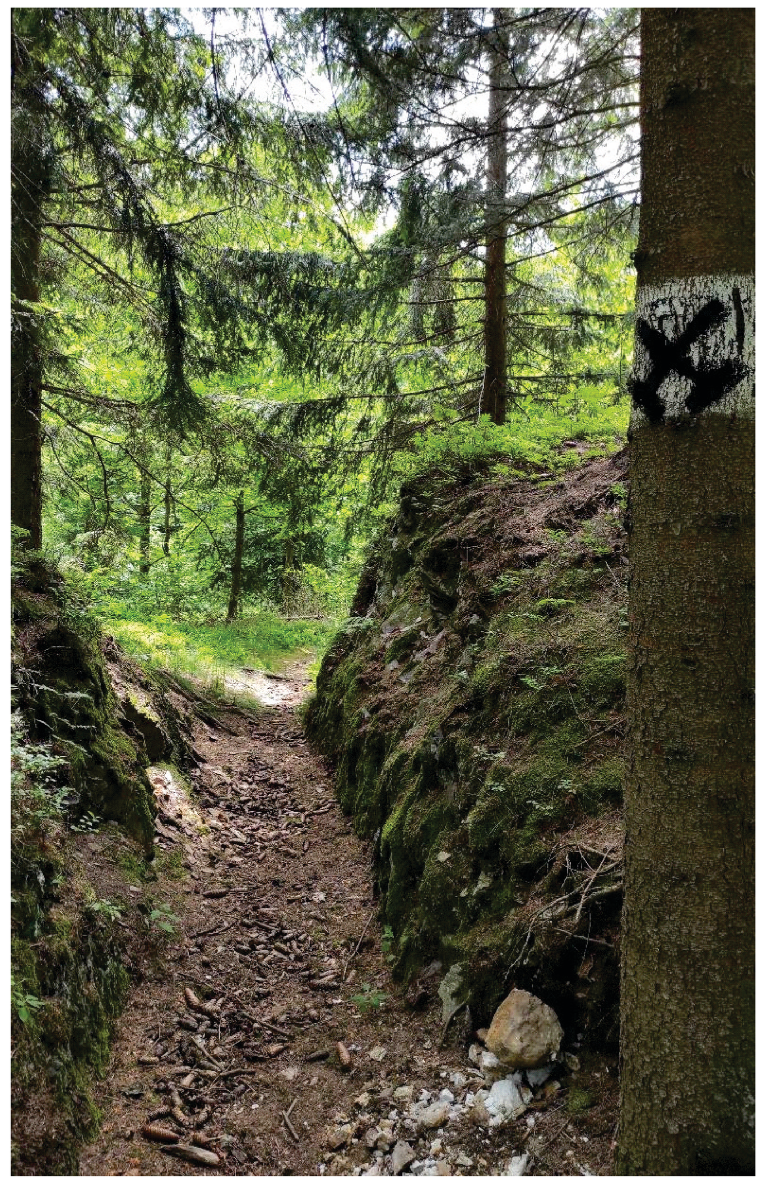

Figure 2. Exploration trench in the Przecznica area.

Analytical methods

Optical light microscopy was used to characterize ore minerals and define textural relationships. Chemical analyses of sulfides, sulphosalt and tellurides were carried out using a JEOL JXA-8230 Super-Probe electron microprobe at the Laboratory of Critical Elements AGH-KGHM in Kraków. The microprobe was operated in the wavelength-dispersion mode at an accelerating voltage of 20kV and probe current of 20 nA. The following standards and spectral lines were used for sulfides and sulphosalts: pyrite (FeKα, SKα), chalcopyrite (CuKα), sphalerite (ZnKα), Ag (AgLα), In2Se3 (InLα), stibnite (SbLα), Co (CoKα), CdS (CdLα) Bi2S3 (BiMα), galena (PbMα), Bi2Te3 (TeLα), GaAs (AsLα), Sb2Se3 (SeLα) and SnS (SnLα). Electron microprobe data were corrected using the ZAF procedure and JEOL software.

Psi Grzbiet area

The sulfide assemblage near the "Psi Grzbiet Mine" is dominated by chalcopyrite, forming irregular, 0.1-5 mm grains/blebs and disseminations in quartz and mica-schist; in some cases accompanied by sphalerite.

Tellurides are rare in this area, with only two occurrences identified during this study. These were one grain of joseite-A ($Bi_4(S,Te)_3$) intergrown with native-Bi and pyrrhotite in chalcopyrite and one small grain of hedleyite (Bi_7Te_3) next to cassiterite in a sulfide-free sample.

Identified silver-bearing minerals include freibergite (Ag apfu (atoms per formula unit)> 4) and Ag-rich tetrahedrite (Ag apfu < 4) (Fig. 3A, Table 1), galena (0.26-1.48 wt. % Ag), unidentified Pb-Sb-Bi sulphosalts containing 8-9.8 wt.% Ag, and a phase with a chemical composition of Te-rich canfieldite ($Ag_8Sn(S,Te)_6$). This latter rare phase has been previously identified in Poland by the authors in a pyrite-pyrrhotite-sphalerite association in hornfels from the "Sztolnie Żaby" (unpublished data) in the Szklarska Poręba Belt (Fig. 3B, Table 2).

Ullmannite NiSbS and garavellite $FeSbBiS_4$ occur as inclusions and small grains (20-200 um) in chalcopyrite. Native-Bi, Pb-Bi-Sb sulphosalts and Bi oxide intergrowths form needle like-shapes (0.2-3 mm long) in quartz and sometimes in chalcopyrite. Strong alteration and the presence of bismuth oxides suggest they might represent a remnant of primary sulphosalt mineralization which broke down during regional metamorphism.

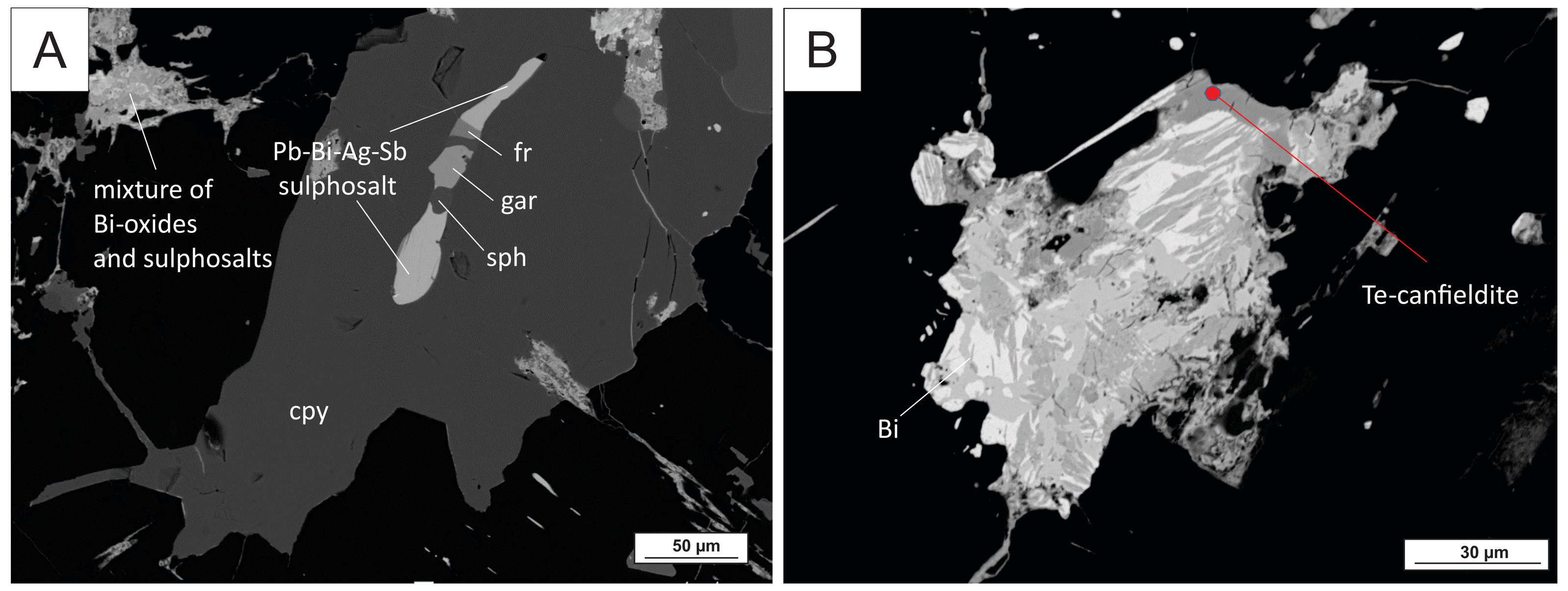

Figure 3. Example of Ag-tetrahedrite (fr), garavellite (gar) and Pb-Bi-Sb-Ag sulphosalt association with chalcopyrite (cpy) and sphalerite (sp), sample PG 2B (A) and Te-canfieldite with native Bismuth (Bi) sample PG 2A (B) from Psi Grzbiet area, BSE images.

Table 1. Composition (in wt. %) of members of the freibergite series "freibergite-(Fe)" from the Psi Grzbiet area.

	PG2B 5a/5	PG2A 10/1	PG2B 5a/3	PG2A 5a/3	PG1 3a/1	PG2A1/1	PG2B 6a/5
Ag	35.88	30.07	29.07	24.27	22.48	20.59	20.20
S	20.30	21.79	21.47	22.81	22.87	23.36	23.05
Fe	4.97	5.81	5.54	5.59	5.62	5.59	5.58
Cu	12.01	16.62	16.52	20.96	22.15	23.26	23.32
Bi	0.21	0.05	0.22	0.23	0.17	0.32	0.46
Te	0.42	<0,03	0.18	0.20	0.11	0.12	<0,03
Pb	0.16	<0,06	0.36	0.13	0.08	0.13	0.08
Sb	25.66	26.28	26.42	26.13	26.53	27.11	26.80
Zn	0.66	<0,05	0.54	0.83	0.98	0.93	0.94
As	0.13	<0,12	0.13	<0,12	0.14	0.16	0.13
Se	0.16	<0,13	<0,13	<0,13	<0,13	<0,13	<0,13
Total	100.56	100.62	100.43	101.16	101.12	101.56	100.57
apfu Σ29 atoms							
Ag	6.55	5.25	5.11	4.08	3.76	3.40	3.37
S	12.46	12.79	12.70	12.91	12.87	12.98	12.93
Fe	1.75	1.96	1.88	1.82	1.81	1.78	1.80
Cu	3.72	4.92	4.93	5.99	6.29	6.52	6.60
Bi	0.02	0.00	0.02	0.02	0.01	0.03	0.04
Te	0.07	0.00	0.03	0.03	0.01	0.02	0.00
Pb	0.02	0.00	0.03	0.01	0.01	0.01	0.01
Sb	4.15	4.06	4.11	3.89	3.93	3.97	3.96
Zn	0.20	0.00	0.16	0.23	0.27	0.25	0.26
As	0.03	0.03	0.03	0.02	0.03	0.04	0.03
Se	0.04	0.00	0.00	0.00	0.00	0.00	0.00

Przecznica area

Tin-sulfides are represented by stannite in samples from the Przecznica area where it is present in a chalcopyrite-sphalerite-rich assemblage and sometimes intergrown with arsenopyrite and cobaltite (Fig. 4 & 5).

Cobaltite is the most abundant carrier of Co, followed by Co-bearing arsenopyrite (Fig. 6.). Glaucodot, ullmannite and Fe-Ni diarsenide also contain Co but were rarely observed.

The most significant difference between arsenopyrites from both areas of investigation is a slight admixture of Ni (0.35-0.73 wt.%) in arsenopyrite from the Psi Grzbiet in comparison with low Ni content in those from Przecznica (in all samples <0.07 wt.%).

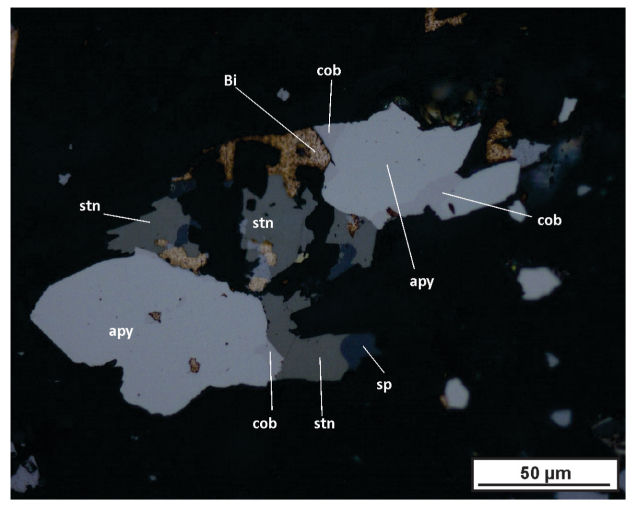

Figure 4. Association of Co-containing arsenopyrite (apy), cobaltite (cob), stannite (stn), sphalerite (sp) and native Bi (Bi), Przecznica area, sample PAM 2B 06,

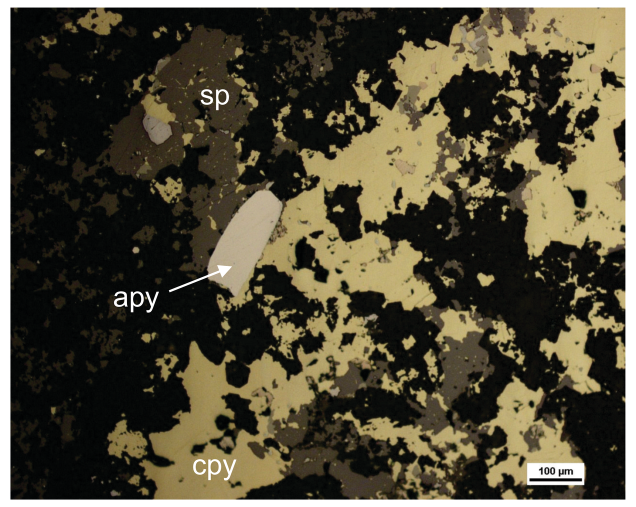

Figure 5. Co-bearing arsenopyrite (apy) with chalcopyrite (cpy) and sphalerite (sp), sample PAM 2B 05, reflected light.

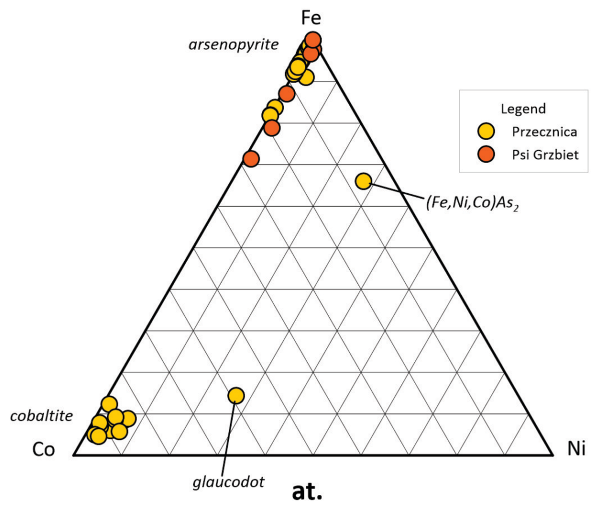

Figure 6. Ternary Ni-Co-Fe plot of Co-bearing minerals from the Przecznica and Psi Grzbiet area.

	PG_1	PG_2	SŻ	Len.
Ag	62.09	61.07	64.15	63.26
S	9.51	9.8	10.91	9.23
Fe	<0.04	<0.04	0.23	na
Cu	<0.05	<0.05	<0.05	0.01
Te	17.09	16.66	11.23	18.15
Bi	0.35	0.21	<0.05	na
Ge	na	na	na	0.04
Pb	1.27	4.63	na	na
Sn	8.12	7.67	8.26	8.88
Sb	<0.03	<0.03	<0.03	na
Zn	<0.04	<0.04	1.64	0.03
As	<0.1	<0.1	<0.1	na
Se	0.27	0.12	3.28	0.05
Total	98.7	100.16	99.69	99.65

Table 2. Comparison of analyses (in wt.%) of Te-rich canfieldite from the Psi Grzbiet and the Sztolnie Żaby, with average composition of this phase from the Lengenbach.

Discussion and conclusions

While Co and Sn constitute the focus of historical mining activity in the Psi Grzbiet and St. Maria-Anna mines, diverse mineralogy including rare Te-canfieldite (reported only in a handful of localities worldwide), "freibergite-(Fe)", garavellite, hedleyite, joseite-A, ullmannite, native Bi, galena, cobaltite, stannite, arsenopyrite and glaucodote, demonstrate the polymetallic character of the ore and mineralizing processes. Psi Grzbiet ore is characterized by the presence of Ag, Ni, Sb, and Te minerals with a small amount of As-bearing phases (represented by arsenopyrite) while the mineralogy of the Przecznica area is characterized by an abundance of As phases (mainly cobaltite and arsenopyrite).

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References

Bindi L, Nestola F, Guastoni A, Zorzi F, Peruzzo L, Raber T (2012). Te-rich canfieldite, Ag8Sn(S,Te)6, from the Lengenbach quarry, Binntal, Canton Valais, Switzerland: occurrence, description and crystal structure. Can Min 50:111-118; Mazur S, Aleksandrowski P, Szczepiński J (2010) Zarys budowy i ewolucji tektonicznej waryscyjskiej struktury Sudetów. Przegląd Geologiczny 58(2):133-145; Michniewicz M, Bobiński W, Bobiński W, Siemiątkowski J (2006) Mineralizacja cynowa w środkowej części pasma łupkowego Starej Kamienicy (Sudety zachodnie): Prace Panstwowego Instytutu Geologicznego 185:1-136; Mikulski SZ (2007). Metal ore potential of the parent magma of granite–the Karkonosze massif example. Granitoids in Poland. Archivum Mineralogiae, Monogr 1:123-145; Mikulski SZ, Williams IS, Stein H J, Wierchowiec J (2020). Zircon U-Pb dating of magmatism and mineralizing hydrothermal activity in the Variscan Karkonosze Massif and Its eastern metamorphic cover (SW Poland). Minerals 10(9):787.; Mochnacka K, Oberc-Dziedzic T, Mayer W, Pieczka A (2015). Ore mineralization related to geological evolution of the Karkonosze–Izera Massif (the Sudetes, Poland)—towards a model. Ore Geol Rev 64:215-238; Piestrzyński A, Mochnacka K (2003) Discussion on the sulphide mineralization related to the tin-bearing zones of the Kamienica schists belt (western Sudety Mountains, SW Poland) in Sudety Zachodnie - od wendu do czwartorzędu, Ciężkowski W, Wojewoda J Żelaźniewicz A (eds), Wind, Wroclaw 169-182.